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Fluorescence Modulation in Triphenyl Pyrazoline- and Azobenzene-Based Side-Chain Polymethacrylate

Liang Zhang[1, *], **Feng Zhang**[2], **Qi Liu**[1]

[1]School of Material Science and Engineering, Yancheng Institute of Technology, Yancheng, China
[2]Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng, China

Email address
zhangliang@ycit.edu.cn (Liang Zhang)
[*]Corresponding author

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Abstract: A novel polymethacrylate derivative, poly(4-(2,5-diphenyl-3,4-dihydro-2H-pyrazol-3-yl)-phenyl methacrylate-*co*-4-methacryloyloxyazobenzene) [PDPMA-*co*-PMOAB], was synthesized and characterized *via* ^{1}H NMR. The copolymer combined the photoluminescence and photochemical behavior of both triphenyl pyrazoline and azobenzene moieties in the side chains. The photoluminescence property of the polymer so obtained could be modified through the photochemical isomerization reaction of the photoactive groups. The copolymer showed good solubility in common solvents such as acetone, dichloromethane, and tetrahydrofuran (THF). The composition of DPMA/MOAB (mol/mol) in the copolymer was also calculated from ^{1}H NMR, and the ratio was 0.78:1. The UV-vis spectrum of PDPMA-*co*-PMOAB showed an overlap band of the pyrazoline moiety and azobenzene moiety (π-π* transition) at 336 nm and a band at 450 nm attributed to the n-π* transition band of azobenzene. Spectral changes accompanied the photochemical conversion of trans–cis form on irradiation of PDPMA-*co*-PMOAB at UV light 365 nm in THF solution. Meanwhile, the emission was enhanced by eightfold after irradiation for 16 min.

Keywords: Fluorescence, Pyrazoline, Azobenzene, Trans–cis Isomerization

1. Introduction

At present, research interest in azobenzene-containing polymers is increasing because they can be used in optical data storage [1–4], optical sensors [5–7], and nonlinear optical materials [8–10]. Azobenzene and its derivatives undergo conversion from the trans form to the cis form under irradiation at 365 nm and revert to the trans form under irradiation at 450 nm or in the dark. This photoisomerization leads to a photostationary equilibrium [11]. Photoisomerization of azobenzene in the side chain of polymer has been monitored to study the change in conjugated main-chain emission. Harbron et al. [12–16] investigated the manipulation of the fluorescence properties of a family of polymer poly(p-phenylenevinylene) (PPVs) via side-chain azobenzene photoisomerization. Their findings represented an initial step toward defining practical design considerations for photomodulated PPV derivatives. Zhao et al. [17] studied the structure dependence of photochromism, which originated from a combination of conjugated polythiophene backbone and photoactive side-chain azobenzene group. The fluorescence intensity was found to decrease with UV irradiation for the polymer. Kannan et al. [18] synthesized two series of liquid crystalline polymers containing stilbene and α-methylstilbene in the main chain and terminally substituted azobenzene moiety in the side chain. The emission spectra of all the polymers excited at 350 nm at different time intervals (30 s) showed a decrease in intensity.

To investigate the effect of isomerization of azobenzene moieties in the side chain on the fluorescence originating from the side chain [19, 20], we synthesized the copolymer PDPMA-co-PMOAB, in which both triphenyl pyrazoline [21–26] and azobenzene moieties were connected to the flexible main chain. The fluorescent spectra of the polymer showed that the emission intensities could be modulated through irradiation with UV light. The copolymer can be potentially applied to detect surface relief gratings (SRG) because fluorescence detection offers one of the most sensitive techniques for detecting microscopic events, such as molecular migration [27].

2. Materials and Methods

2.1. Regents and Solvents

Methacryloyl chloride (≥98%, Haimen Best Fine Chemical Co. Ltd) was distilled under vacuum before use. Azobisisobutyronitrile (AIBN, CP; Shanghai Chemical Reagent Co., Ltd.) was purified through recrystallization from ethanol. 3-(4-Hydroxyphenyl)-1-phenylprop-2-en-1-one and 4-(2,5-diphenyl-3,4-dihydro-2H-pyrazol-3-yl)-phenol were synthesized according to the previously reported methods [28, 29]. 4-Methacryloyloxyazobenzene was prepared following a previously reported procedure [30]. Other agents were used as received.

2.2. Measurements

Conversions of monomer were determined by gravimetry. ^{1}H NMR spectra were measured using INOVA 400 MHz NMR spectrometer, $CDCl_3$ as solvent, and tetramethylsilane as the internal standard at ambient temperature. Molecular weights and the polydispersity relative to PMMA were determined on Waters 1515 GPC with tetrahydrofuran (THF) as solvent at a flow rate of 1 mL/min with column temperature of 30 °C. UV-vis absorption spectra of initiator, monomer, and polymer in THF solutions were determined on a Shimadzu RF540 spectrophotometer. Room temperature emission and excitation spectra were obtained using Edinburgh-920 fluorescence spectrophotometer. The purity was determined with a Waters 515 HPLC apparatus: a mixture of methanol and water (methanol: water = 80: 20, v/v) was used as the eluent at a flow rate of 0.8 mL/min at 30°C with a C18 column and Waters 996 detector.

2.3. Synthesis of 4-(2, 5-diphenyl-3, 4-dihydro-2H-pyrazol-3-yl)-phenyl Methacrylate

Approximately 3.1 g of 0.01 mol 4-(2,5-diphenyl-3,4-dihydro-2H-pyrazol-3-yl)-phenol was dissolved in a mixture of Et_3N (2.0 g, 0.02 mol) and THF (80 mL) and then cooled with an ice-water bath. A solution of methacryloyl chloride (1.0 g, 0.01 mol) in 20 mL of THF was added dropwise under a nitrogen atmosphere. The mixture was stirred for 1 h and the ice-water bath was removed. The reaction was stirred continuously for 24 h at room temperature, and the solution was filtered and poured into water. The precipitated product was purified through a column of silica gel using a mixed solvent of petroleum ether and ethyl acetate (V: V = 5: 1) as eluent.

Yellow solid. Yield: 77%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.75-7.72 (d, 2H), 7.42-7.30 (m, 11H), 6.85-6.79 (m, 1H), 6.33 (s, 1H), 5.76 (s, 1H), 5.32-5.27 (dd, 1H), 3.88-3.81 (dd, 1H), 3.20-3.14 (dd, 1H), 2.05 (s, 3H).

The purity exceeded 98% as determined via HPLC.

2.4. Synthesis of Polymers

In a general procedure, cyclohexanone (monomer/cyclohexanone = 1: 5 $g \cdot mL^{-1}$), initiator, and monomer were mixed in a round-bottom flask. Polymerization was conducted at 70°C under N_2 atmosphere for 10 h. Subsequently, the samples were diluted with THF and precipitated through the addition of a mixture of ethyl acetate and methanol ($V_{ethyl\ acetate}/V_{methanol}/V_{THF} = 5/5/1$). Reprecipitation was conducted three times and the samples were dried under vacuum at room temperature.

3. Results and Discussion

3.1. Synthesis of Polymers

The details of the synthesis are given in the experimental section. The molecular weight and the polydispersity indices (PDIs) of all the polymers are listed in Table 1. The structure of PDPMA-*co*-PMOAB is shown in Figure 1. The copolymer showed good solubility in acetone, dichloromethane, and THF. The polymer was purified by repeated reprecipitation from a mixture of ethyl acetate and methanol. As shown in Figure 1, the resonances at approximately 5.80 and 6.30 ppm, related to the vinylidenic protons of monomers DPMA and MOAB, respectively, were absent, suggesting that the copolymer was pure for photochemical studies. The composition of DPMA/MOAB (mol/mol) in the copolymer was calculated from ^{1}H NMR, and the ratio was 0.78:1.

Table 1. *Number average molecular weight [$M_{n,(GPC)}$s] and polydispersity indices (PDIs) of PDPMA, PMOAB, and PDPMA-co-PMOAB.*

Sample	Initial Feed (DPMA:MOAB:AIBN) (mol/mol)	$M_{n,(GPC)}$s (g/mol)	PDIs
PDPMA	50:0:1	7200	1.96
PMOAB	0:50:1	8000	1.55
PDPMA-*co*-PMOAB	50:50:1	10300	1.75

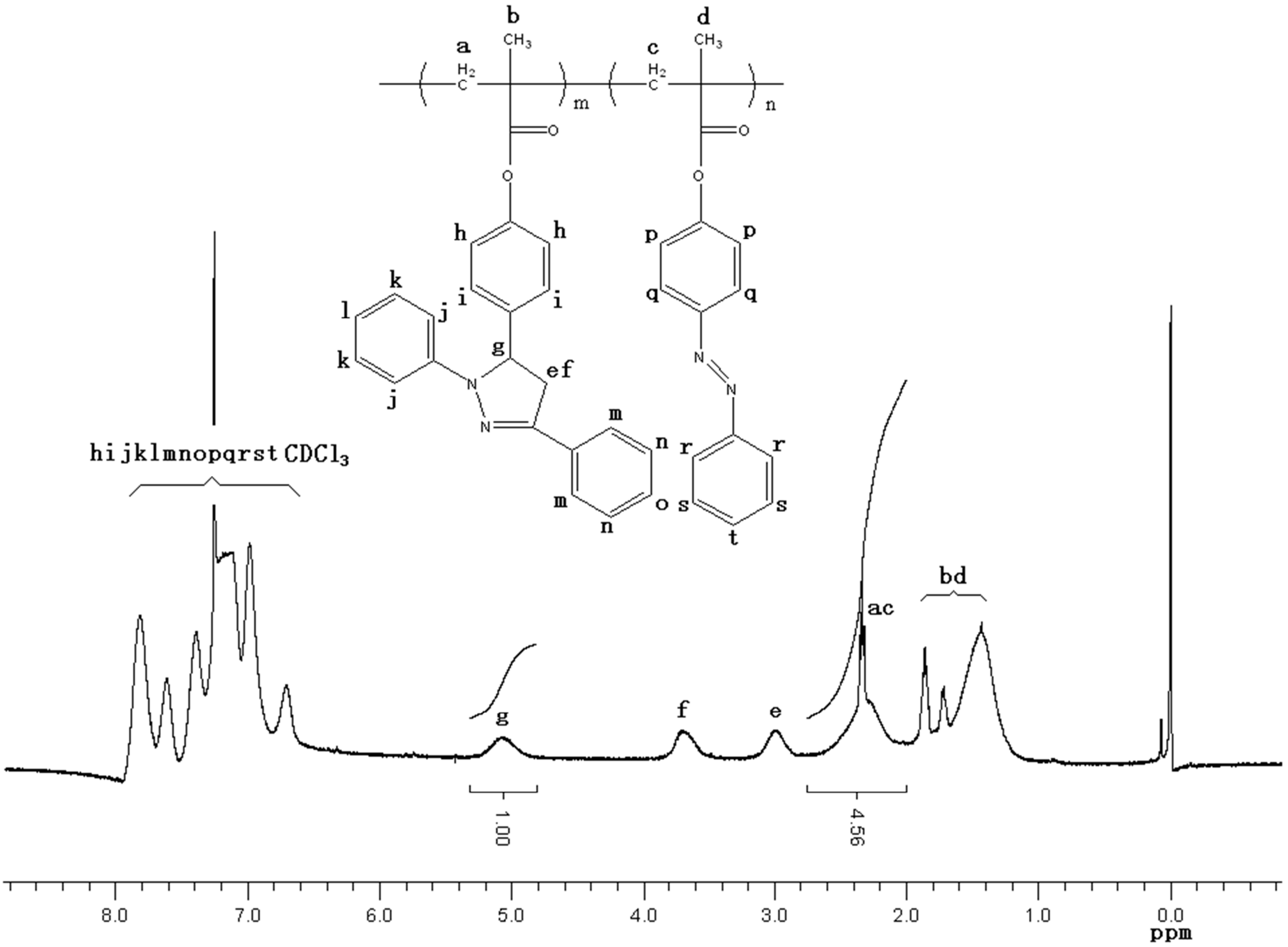

Figure 1. ^1H *NMR spectrum of PDPMA-co-PMOAB.*

3.2. UV-vis Absorption Spectra

The UV-vis spectra of PMOAB, PDPMA, and PDPMA-*co*-PMOAB are shown in Figure 2. The absorption maxima for PMOAB were observed with two wavelengths 325 and 450 nm, respectively. The absorption band at 325 nm was related to the π-π* transition of the azobenzene unit and the weak absorption band at 450 nm was the low-energy n-π* transition of the azobenzene unit. The trans form was more stable, and the percentage of the cis form was negligible compared with that of the trans form under normal conditions. PDPMA showed absorption maxima wavelength at 360 nm with a shoulder peak at 310 nm. The UV-vis spectrum of PDPMA-*co*-PMOAB showed an overlap band of the pyrazoline moiety and azobenzene moiety (π-π* transition) at 336 nm and a band at about 450 nm attributed to the n-π* transition band of azobenzene.

The spectral changes accompanying the photochemical conversion of trans–cis form on irradiation of PDPMA-*co*-PMOAB at UV light 365 nm (power: 8 W, lamp source: mercury lamp) are shown in Figure 3. Photoirradiation in solution was carried out in THF solution, and the temperature was maintained at 25°C to inhibit thermal cis–trans isomerization. PMOAB demonstrated strong absorption in the region from 300 nm to 400 nm (Figure 2), which was attributed to the π-π* transition bands of the trans-azobenzene units. Thus, irradiation at 300 nm < λ < 400 nm should be effective in trans-to-cis photoisomerization. On irradiation of the polymer solution at different time intervals, the azobenzene chromophores underwent trans–cis photoisomerization. On trans–cis isomerization, the intense absorption band at 330 nm decreased, and absorption at 450 nm increased in unequal proportions.

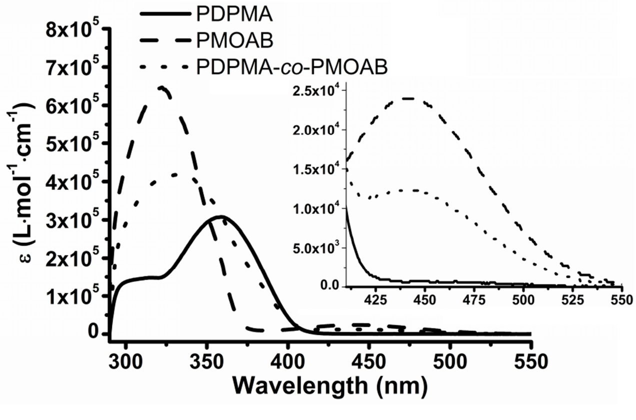

Figure 2. UV-vis spectra of PMOAB (3.3×10^{-6} *mol/L), PDPMA (5.3×10*$^{-6}$ *mol/L) and PDPMA-co-PMOAB (3.1×10*$^{-6}$ *mol/L) in THF solution.*

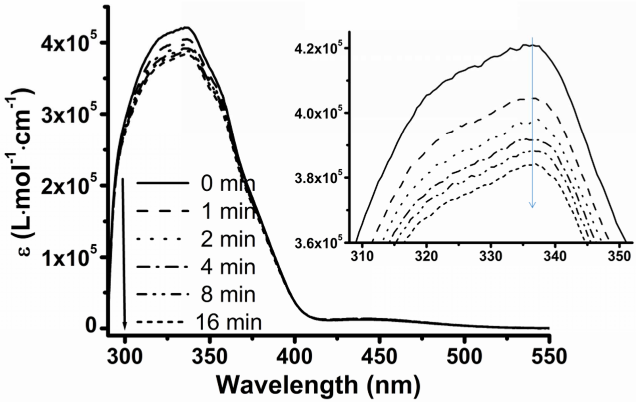

Figure 3. *UV-vis spectra of PDPMA-co-PMOAB (3.1×10^{-3} mol/L) in THF solution with different irradiation times through UV light at 365 nm.*

3.3. Fluorescence Emission Spectra

Generally, azobenzene molecules did not show appreciable emission due to the trans–cis isomerization processes, leading that no shallow minima for low-lying excited states were present for both the trans and cis configurations [31]. As shown in Figure 4, PMOAB emitted very weak fluorescence in THF solution. In the case of the homopolymer PDAMA, it emitted strong blue fluorescence in THF solution because pyrazoline unit is a typical fluorescent chromophore. Compared with the homopolymer PDAMA, the fluorescence of the copolymer PDPMA-*co*-PMOAB was weak and quenched a lot due to PET bwtween triphenyl pyrazoline and azobenzene moieties which would dramatically quench the fluorescence of triphenyl pyrazoline units.

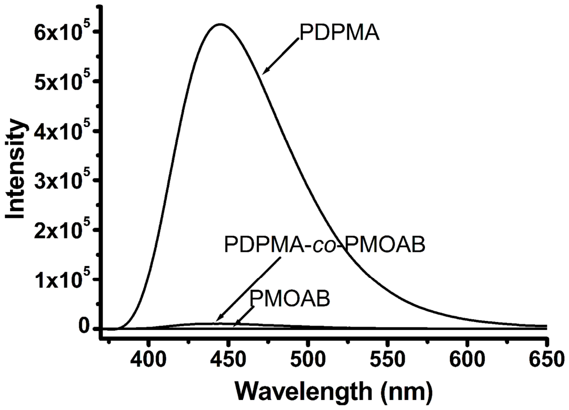

Figure 4. *Fluorescence emission spectra of PMOAB (3.3×10^{-6} mol/L), PDPMA (5.3×10^{-6} mol/L) and PDPMA-co-PMOAB (3.1×10^{-6} mol/L) in THF solution (λ_{ex} = 336 nm).*

Further, the effect of photoisomerization of azobenzene groups on the fluorescence properties of the copolymer PDPMA-*co*-PMOAB was also investigated because electron transfer process between trans-azobenzene and triphenyl pyrazoline is different from that between cis-azobenzene and triphenyl pyrazoline. Upon irradiation through UV light of 365 nm, the photoluminescence intensity of the copolymer was increased with increasing the irradiation time in THF solution (Figure 5). The photoluminescence intensity was enhanced by eight fold after irradiation for 16 min because some trans-azobenzene units transferred to cis-azobenzene units which could decrease the photoinduced electron transfer (PET) between azobenzene units and pyrazolines because the cis isomer formed on irradiation was non planar [27, 32]. The lone pair electrons on nitrogen could no longer effectively conjugate with the π-electrons of the fluorophore, thereby inhibiting the PET mechanism.

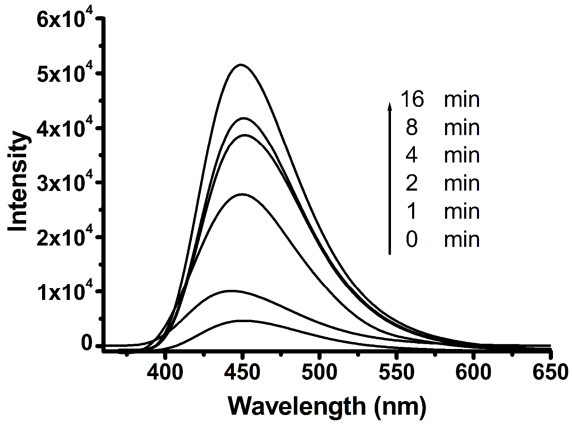

Figure 5. *Fluorescence emission spectra of PDPMA-co-PMOAB (3.1×10^{-6} mol/L mg/L) in THF solution with different irradiation times through UV light at 365 nm (λ_{ex} = 336 nm).*

4. Conclusion

Polymethacrylate composed of fluorescence pyrazoline chromophore and photoresponsive azobenzene moiety was synthesized. The fluorescent spectra of the polymer showed that the emission intensities could be modulated by irradiation with UV light. The copolymer can be potentially applied to detecting surface relief gratings.

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References

[1] Spiridon MC, Iliopoulos K, Jerca FA, Jerca VV, Vuluga DM, Vasilescu DS, Gindre D, Sahraoui B. Novel pendant azobenzene/polymer systems for second harmonic generation and optical data storage. Dyes Pigments. 2015; 114: 24–32.

[2] Hu DQ, Lin JZ, Jin S, Hu YL, Wang WJ, Wang RR, Yang B. Synthesis, structure and optical data storage properties of silver nanoparticles modified with azobenzene thiols. Mater Chem Phys. 2016; 170: 108–12.

[3] Berberova N, Daskalova D, Strijkova V, Kostadinova D, Nazarova D, Nedelchev L, Stoykova E, Marinova V, Chi CH, Lin SH. Polarization holographic recording in thin films of pure azopolymer and azopolymer based hybrid materials. Opt Mater. 2017; 64: 212–6.

[4] Wang XL, Wang XG. Photoinduced self-structured surface patterns on films of epoxy-based polymers containing trifluoromethyl-substituted azo chromophores. Acta Polymerica Sinica. 2012; 012: 207–14.

[5] Wang XQ, Liu XY, Wang XG. Surface-relief-gratings based on molecularly imprinted polymer for 2,4-dichlorophenoxyacetic acid detection. Sensor Actuat B-chem. 2015; 220: 873–9.

[6] Wang XQ, Liu XY, Wang XG. Hydrogel diffraction grating as sensor: A tool for studying volumephase transition of thermo-responsive hydrogel. Sensor Actuat B-chem. 2014; 204: 611–6.

[7] Wang XQ, Ye G, Wang XG. Hydrogel diffraction gratings functionalized with crown ether for heavy metal ion detection. Sensor Actuat B-chem. 2014; 193: 413–9.

[8] Li NJ, Lu JM, Xia XW, Xu QF, Wang LH. Synthesis and the third-order nonlinear optical properties of soluble polymers with different substituted azobenzene side chains. Polymer. 2009; 50: 428–33.

[9] Li NJ, Lu JM, Xia XW, Xu QF, Wang LH. Synthesis of third-order nonlinear optical polyacrylates containing an azobenzene side chain via atom transfer radical polymerization. Dyes Pigments. 2009; 80: 73–9.

[10] Li NJ, Lu JM, Xu QF, Wang LH. Synthesis and the third-order non-linear optical properties of new azobenzene-containing side-chain polymers. Opt Mater. 2006; 28: 1412–6.

[11] Shinkai S, Manabe O. Photocontrol of ion extraction and ion transport by photofunctional crown ethers. Top Curr Chem. 1984; 121: 67–104.

[12] Grimes AF, Call SE, Vicente DA, English DS, Harbron EJ. Toward efficient photomodulation of conjugated polymer emission: optimizing differential energy transfer in azobenzene-substituted PPV derivatives. J Phys Chem B. 2006; 110: 19183–90.

[13] Harbron EJ, Vicente DA, Hoyt MT. Fluorescence modulation via isomer-dependent energy transfer in an azobenzene-functionalized Poly(phenylenevinylene) derivative. J Phys Chem B. 2004; 108: 18789–92.

[14] Harbron EJ, Vicente DA, Hadley DH, Imm MR. Phototriggered fluorescence color changes in azobenzene-functionalized conjugated polymers. J Phys Chem A. 2005; 109: 10846–53.

[15] Grimes AF, Call SE, Harbron EJ, English DS. Wavelength-resolved studies of förster energy transfer in azobenzene-modified conjugated polymers: the competing roles of exciton migration and spectral resonance. J Phys Chem C. 2007; 111: 14257–65.

[16] Lewis SM, Harbron EJ. Photomodulated PPV emission in a photochromic polymer film. J Phys Chem C. 2007; 111: 4425–30.

[17] Zhao XY, Wang MZ, Liu HJ. Structure dependence of photochromism of azobenzene-functionalized polythiophene derivatives. *J Appl Polym Sci.* 2008; 108: 863–9.

[18] Rameshbabu K, Kannan P. Investigation on stilbene- and azobenzene-based liquid crystalline organophosphorus polymers. J Appl Polym Sci. 2007; 104: 2760–8.

[19] Ren H, Chen D, Shi Y, Yu HF, Fu ZF. Multi-responsive fluorescene of amphiphilic diblock copolymer containing carboxylate azobenzene and N-isopropylacrylamide. Polymer. 2016; 97: 533-42.

[20] Ren H, Chen D, Shi Y, Yu HF, Fu ZF. A carboxylic azo monomer and its homopolymer: synthesis, self-organization and fluorescence behavior in solution. Polym Chem. 2015; 6: 270-7.

[21] Abbas A, Hussain S, Hafeez N, Hasan A, Naseer MM. Synthesis and spectral characterization of new 1,3,5-triaryl-2-pyrazolines highlighting effect of alkyloxy chain length on fluorescence. Spectrochim Acta A. 2014; 127: 32–40.

[22] Abbas A, Hussain S, Hafeez N, Hasan A, Naseer MM. Synthesis and spectral characterization of new homologous 1,3,5-triaryl-2-pyrazolines: influence of alkyloxy chain length on fluorescence. Spectrochim Acta A. 2014; 133: 182–9.

[23] Ramkumar V, Kannan P. Highly fluorescent semiconducting pyrazoline materials for optoelectronics. Opt Mater. 2015; 46: 605–13.

[24] Ramkumar V, Kannan P. Thiophene and furan containing pyrazoline luminescent materials for optoelectronics. J Lumin. 2016; 169: 204–15.

[25] Manjunath R, Kannan P. Pyrazoline based fluorescent chemosensor for Al^{3+} ion detection and live cell imaging. New J Chem. 2018; 42: 10891-7.

[26] Ying PZ, Qing HX, Yun SY, Xiao YL, Chun MM, Jia XR, Hui CG. A chromene pyrazoline derivatives fluorescent probe for Zn^{2+} detection in aqueous solution and living cells. Inorg Chim Acta. 2018; 479: 128-34.

[27] Liu LH, Nakatani KT, Pansu R, Vachon JJ, Tauc P, Ishow E. Fluorescence patterning through photoinduced migration of squaraine-functionalized azo derivatives. Adv Mater. 2007; 19: 433–6.

[28] Shriner RL, Kurosawa T. Chalcones. II. decomposition by alkali. J Am Chem Soc. 1930; 52: 2538–40.

[29] Bilgin AA, Palaska E, Sunal R, Gumusel B. Some 1,3,5-triphenyl-2-pyrazolines with antidepressant activities. Pharmazie. 1994; 49: 67–9.

[30] Moniruzzaman M, Sabey CJ, Fernando GF. Synthesis of azobenzene-based polymers and the in-Situ characterization of their photoviscosity effects. Macromolecules. 2004; 37: 2572–7.

[31] Rau H. Spectroscopic properties of organic azo compounds. Angew Chem Int Ed. 1973; 12: 224–35.

[32] Bissell RA, Silva AP, Gunaratne HQN, Lynch PLM, Maguire GEM, McCoy CP, Sandanayake KRAS. Fluorescent PET (photoinduced electron transfer) sensors. Top Curr Chem. 1993; 168: 223–64.